Dependence of morphology, dispersion and hydrodesulfurization performance of active phases in NiMo/SBA-15 on loading method

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Abstract: The effect of loading method on the morphology, dispersion and hydrodesulfurization (HDS) performance of NiMo/SBA-15 catalysts is systematically examined. The results revealed that with the newly proposed Mo-based hybrid nanocrystals as precursors, metal species could be effectively isolated from each other and dispersed well over SBA-15 even at high loading amounts, which helped to form MoS_2 with short length and suitable stacking layers and resulted in a remarkably enhanced activity. By contrast, poorly dispersed MoS_2 slabs with overlong length and ultra-high stacking layers were obtained by conventional incipient wetness impregnation because of the weak metal-support and strong metal-metal interaction.

Keywords: NiMo/SBA-15, hydrodesulfurization, loading method.

1. Introduction (11-point boldface)

The production of ultralow-sulfur fuels has become the theme of the current oil refining industry. Nowadays, fuel desulfurization still mainly depends on hydrodesulfurization (HDS) technique, therefore the development of novel HDS catalysts and processes to improve the desulfurization efficiency has attracted more and more attention [1]. Recently, we proposed a novel strategy to fabricate Mo catalysts supported over γ-Al_2O_3 by using Mo-based inorganic-organic hybrid nanocrystals (HNCs) instead of Mo-anions as precursors and such HNCs possess stable core-shell structure with polyoxomolybdate anions as the inorganic core and long-chain quaternary ammonium cations as the organic shell [2-5]. Herein, we extend this loading strategy to prepare SBA-15-based NiMo catalysts with different amounts of MoO_3 (13 and 19 wt.%) and by comparison, another two NiMo/SBA-15 catalysts with the same loadings are obtained through the conventional incipient wetness impregnation method. The dependence of morphology, dispersion and HDS performance of active phases on loading method is systematically investigated.

2. Experimental (or Theoretical)

The mesoporous silica SBA-15 was synthesized according to the previously published procedure. NiMo/SBA-15 catalysts with different MoO_3 contents (13 and 19 wt.%) were prepared by two methods, respectively. One is our newly proposed Mo-based hybrid nanocrystals as precursors preparation strategy (denoted as HA-cat) and the other one is conventional incipient wetness impregnation method (labeled as IM-cat). The HA method mainly followed the preparation route in references [2-4] but with some minor adjustments. The HDS activity of the catalysts was assessed in a continuously flowing tubular fixed-bed microreactor using 1 wt.% dibenzothiophene (DBT) in heptane as a model compound. All catalysts were presulfided in situ with a mixture of 3 wt.% CS_2 in cyclohexane at 360 ^{o}C for 3 h. After sulfidation, HDS reaction was carried out under the condition of 360 ^{o}C, weight hourly space velocity (WHSV) 22 h^{-1}, volumetric H_2/hydrocarbon ratio 300, and total pressure 4.0 MPa.

3. Results and discussion

In case of a low MoO_3 loading (e.g. < 13 wt.%), both the IM and HA methods produce a well distribution of active species over SBA-15 due to its large surface area. However, when the metal oxides content is high (e.g. 19 wt.% as encountered in our case), the weak metal-support interaction as well as the strong metal-metal interaction will lead to the severe aggregation of metal oxides during the IM process as shown in Figure 1B, giving rise to the poor-distributed active phases with large size and ultra-high stacking layers (Table 1). Such a morphology of MoS_2 slabs reduces the efficiency and accessibility of the active phases, which is the reason for the lowest HDS activity of IM-cat-19. It should be noted that the interaction between the metal species becomes remarkable at high metal concentrations so that it further exacerbates the migration and conglomeration of the metal oxides in the IM process. By contrast, in the HA approach, Mo-based HNCs as the precursors which polyoxomolybdate anions are surrounded by the organic molecules (e.g. CTAB) to form a core-shell structure can isolate the Mo species from each other and effectively diminish the interaction between Mo complexes and thereby prevent the redistribution and agglomeration of the active phases and greatly improve the dispersion of active phases in the pores of SBA-15 (Figure 1A). Owing to the protection of the organic shells, highly dispersed MoS_2 nanoslabs with short length and suitable stacking layers in NiMo/SBA-15 catalysts can be acquired even at high MoO_3 loadings and thus HA-cats have a much higher activity than IM-cats (Table 1).

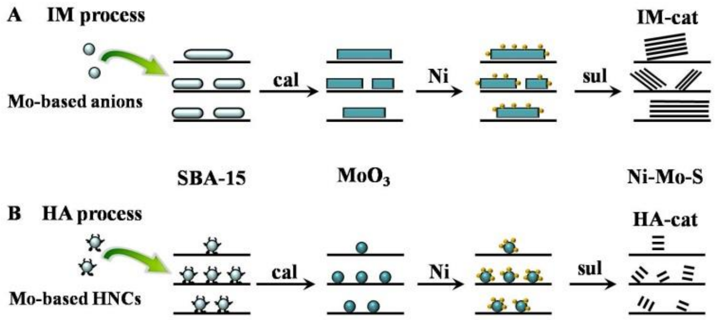

Figure 1. Schematic diagram of the different loading processes.

Table 1. Average stacking layer numbers, length and the fraction of Mo atoms on the edge surface (fMo) of MoS2 crystallites for the four sulfided catalysts and their HDS ratios.

Catalyst	MoS_2 morphology parameter			HDS ratio (%) (T=12 h)
	L	N	f_{Mo}	
IM-cat-13	4.1	4.5	0.28	88.3
IM-cat-19	9.6	16	0.19	66.8
HA-cat-13	3.1	3.5	0.41	95.0
HA-cat-19	3.2	3.8	0.38	98.5

4. Conclusions

HA method is beneficial to acquire a well dispersed active phases over the support and favorable to modulate both the metal-support and metal-metal interaction, and such advantage is more evident and highlighted in the high metal oxides loadings.

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